A Colorimetric Determination

of

Hydrocyanic Acid.

Thesis

by

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The object of this investigation is to devise a rapid, fairly accurate, colorimetric analysis for HCN to be used in field work for determining instantaneous concentrations of the gas under fumigating canvas. A large amount of money is expended yearly by the citrus industry of this state in attempting to control and to eradicate the scale pests. Although fumigation with HCN has been practiced for many years, the progress made has been anything but satisfactory. The greater portion of the work has always been carried on by contractors, who in a large number of cases have been very unscrupulous. The materials and labor are very expensive and the growers have been satisfied to adhere to beaten paths and hope for the best results on scale kill with the least attendant foliage injury. One familiar with fumigating, either from the grower's or the operator's view point, knows that very widely varying results are obtained, even under what are apparently identical conditions. Even after discounting for the dishonesty of some operators and the prejudices of the grower, there is still a large variance between desired or expected results and those actually obtained.

The causes for general divergence from the desired or usual results may lie either in the quality (strength) of the materials used or in the weather conditions, which apparently causes varying distributions of the hydrocyanic acid gas under the canvass. Of course, the first is a factor to be controlled by the manufacturer, jobber, or buyer. However, the latter effects are entirely out of the control of the aforementioned parties and are really little understood by even an experienced operator himself. Hence it is apparent that one of the greatest retard-

ing factors to successful fumigation and pest control is the lack of thorough knowledge of the concentration and distribution of the HCN under the canvas with respect to time and weather conditions. The accumulation and intelligent application of a considerable amount of such data would constitute a great step toward further development and perfection of covers, application systems, and perhaps even new fumigants.

In order to obtain economically any quantity of data on the concentration and distribution of the gas at given intervals after its application under the canvas, a fast semiquantitative analysis must be employed for analyzing these instantaneous gas samples. It immediately becomes apparent that a colorimetric analysis would be very useful in such work, if one could be devised which would give a sufficient degree of accuracy over a sufficiently large range of concentrations.

Selection of the Color Reaction.

In an analysis involving the quantitative estimation of a substance by means of colorimetry it is essential that a given quantity of the substance should always produce a given density of color, at least over a workable range of concentrations. It is also essential that the shade of color be the same; for a blue and a blue-green solution cannot be accurately compared. Hence all foreign materials producing color are to be considered detrimental. Since this method is to be used in field analysis, it is highly desirable to reduce all operations to a minimum. All processes involving evaporation, distillation, and long standing are to be avoided.

Considerable work was found to have been done on the qualitative and quantitative estimation of cyanides, colorimetrically. The fact that cyanides and complex cyanides give characteristic color reactions with a large number of organic and inorganic compounds is well known and has been made the basis of the majority of cyanide tests, usually in connection with the so-called test papers. The following were investigated in view of their utilization under the above named conditions:

1. Guaiac Blue test
2. Fe $(SCN)_3$ test*
3. Picric-Soda test*
4. Prussian Blue test.
5. Benzidine Blue test.*
6. O-Toluidine Blue test.
7. Phthalophenone Pink test

Of these (1) was eliminated because of its extreme sensitiveness and susceptibility to foreign materials. The materials are not stable and must be made up fresh daily.

The well known Fe $(SCN)_3$ color produced by the conversion of the $C\bar{N}$ to $S\bar{C}\bar{N}$ was eliminated by virtue of fundamental requirements barring all evaporations, etc.

The standard mahogany colored picric-soda test is said by previous investigators (Fresenius et. al.) to require boiling or prolonged incubation. It is also stated that the color increases upon standing and is a decided function of the temperature.

The Prussian blue test was thoroughly investigated by Veehoever and Johns (J.A.C.S. 37,1915,601). The most vitally interesting points of their work are: (1) It was found that heating was not (as was previously supposed) necessary, if $K_2 F_2$ is used. (2) The use of $FeCL_3$ is unnecessary. (3) It was found that the "influence of concentration was indeed a very important factor. (They) made a series of experiments using 1 mg. of

KCN in each case and concentration ranging from less than 1 cc. to 10 cc. In dilution of 10 cc. less than ½ as much prussian blue was obtained as when the volume was only 1 cc. (They) found that the maximum color was obtained only when the volume to be tested (containing 1 mg. KCN) was not greater than 1.5 cc., while in greater volumes the color decreased with increasing volumes." Since we desired to apply our test over a wide range, usually in lesser concentrations than 1 mg. per cc., it was at once apparent that the Prussian blue test was inapplicable.

The two organic blue tests involve the partial oxidation of aromatic-amido compounds. It would be very surprising if such a reaction were entirely quantitative under the varying conditions of concentration, temperature, etc. to be encountered under the actual operation of such an analysis. For this reason they were discarded in favor of the Castle Meyer test.

The Castle Meyer or Phthalophenone pink test embraces the oxidation of phthalin (the reduction product of phenolphthalein) to phenolphthalein in basic solution, producing the well known pink color. This method, described as a test paper, seemed to be the most promising and was adopted for study.

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2. J. Pharm. Chim. 12 (1915) 74-81
   Jacs. 38 (1916) 1230-5
3. Proc. Roy. Soc. B 82(1910) 524-87.
   Anal. 35(1910) 406, 469-77
5. C.A. 15, 1259.
6. C.A. 15, 1673.

CONSIDERATION OF SPECIFIC REQUIREMENTS.

The theoretical dosage of HCN applied to a covered tree is not a straight line function of the enclosed volume, but is an empirical quantity which is said to produce satisfactory results. It is some function of the enclosed volume and the area of the exposed canvas. Charts have been compiled giving the dosage (units) for covered trees in terms of the distance over, and the distance around a covered tree as measured by figures on the tent itself and with a tape line. If we assume a covered tree a right circular cylinder, which is very nearly approximated in freshly pruned trees, we may obtain the theoretical gas concentrations under different sized trees.*

Let a = distance over tree in feet
and b = distance around tree in feet
Then we have for the enclosed volume

$$V = \frac{b\left(a - \frac{6}{\pi}\right)}{8\pi}$$

The theoretical concentration of gas under any tent in mg. per liter is given by the relationship:

$$C = \frac{\text{units dosage} \times 18 \times \text{sp. gr. HCN} \times 1000}{\text{Vol. (cu. ft.)} \times 28.3}$$

Sp. gr. of 97.5% HCN at 20° C. = .70
1(100 %) unit = 18 cc. HCN

Hence, if we take a representative number of different sized trees, we have as typical:*

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* "A dosage schedule for citrus fumigation with liquid HCN;- 95 - 987 pure, 1920. R.S.Woglum."

a x b - dosage	Vol.(cu. ft.)	Dosage (cc.)	Concentration mg./liter	% by vol.
10x12 - 2 units	35.5 " "	36 "	24.2	2 %
16x25 - 5 units	208. " "	90 "	10.3	.85%
30x40 - 11 units	1100 " "	198 "	4.3	.33%
36x46 - 15 units	1800 " "	270 "	3.6	.30%
42x52 - 21 units	2800 " "	378 "	3.2	.27%
58x78 - 47 units	8000 " "	846 "	2.5	.21%

The proposed method of sampling the air under the tent consisted of drawing the impregnated air through an absorbing bottle by means of a water aspirator. The time of exposure given a tree varies from 40 minutes to one hour. Since instantaneous gas concentrations are desired, it is quite essential that a sample be withdrawn during a relatively short period of time. Since we also have the factor of obtaining complete absorption, there arises the problem of determining experimentally for a given apparatus the minimum allowable time for sampling with complete absorption of the gas. However, for a basis of experimental work, it was assumed that 500 cc. of the air could be withdrawn and washed in 50 cc.of 0.1N NaOH solution with complete absorption of the HCN in a reasonable length of time. It is also reasonable to expect instantaneous concentrations as low as 10 % of the theoretical. Hence from the above calculations and assumptions, it is seen that in actual operations the 50 cc. of NaOH absorbent may contain from .10 to 12 mg. of HCN.

The first two sizes (2-5 unit trees) are exceptionally small. Under ordinary circumstances the amounts would range from .1 to 5 mg. in the 50 cc. of 0.1N NaOH solution. The above data and assumptions constitute the fundamental basis for future experimental work. The points to be investigated in this analysis are:

Accuracy of test under ideal conditions
Effect of concentration of HCN upon the depth of color
Effects due to temperature
Effects due to difference in heights of column
Stability of materials and permanence of color

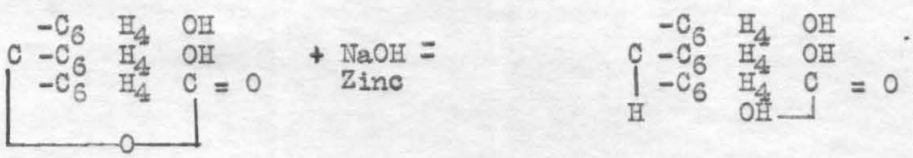
(1) M. Thiery (J. Pharm. Chim. (6) 25 51-53) recommends the use of aluminum in a strongly alkaline solution as a means of reducing phenolphthlein. It was found that this was a very unsatisfactory prodedure. The reduction, as evidenced by the discharge of the characteristic pink color, was very slow, requiring a tremendous excess of metal (both powdered and strip) and prolonged heating for several days to complete the reaction. The resulting mass consisted of thick viscous fluid even after a large excess of water had been added. This material is found to be exceedingly hard to handle in subsequent procedures. It is also of note, contrary to Baeyer (Anal. (202)-81), that there was, what seemed to be, a considerable formation of the further reduction product of phthalin, as shown by its solubility in NaOH and insolubility in a large excess of alcohol. Phthalin is very soluble in alcohol.

Baeyer (Anal. 202-80) recommends zinc in strong caustic solution as a reducing agent. When zinc was employed, the reduction was entirely completed after an hour of gentle heating. None of the further reduced product was apparent upon solution in alcohol in later procedures.

The following procedure was found to be the best for the production of phthalin:

15 grams of phenolphthalein is dissolved in a minimum quantity of hot alcohol, 30 grams mossy zinc and 150 cc. of 15% NaOH solution added. The mixture is heated gently and about 15 grams

zinc dust slowly stirred in. The mixture, which is prepared in a large porcelain dish, is heated for some time after the complete discharge of the pink color, the sides of the dish being washed down to insure the complete reduction of phenolphthalein, as well as to keep the mass workable. The colorless solution is acidified with dilute HCl, the resulting precipitate of phthalin filtered off and washed on a suction filter. The precipitate is quickly dissolved in a minimum quantity of hot alcohol and filtered hot. Hot water is added to the filtrate until the first turbidity is apparent. Phthalin crystalizes out only after very long standing. The precipitated material is filtered and washed in water until entirely free from all traces of unreduced phenol-phthalein, as shown by testing the wash water with NaOH. The precipitate should also give a negative test at this time, as the reduction products are not colored. The moist precipitate is quickly weighed and the moisture determined in an aliquot portion by drying in vacuo or in a non-oxidizing atmosphere. The moist precipitate is immediately dissolved in a known quantity of NaOH solution. To the resulting phthalin test solution which is invariably slightly pink, a small amount of zinc dust is added, the solution heated and filtered. The resulting clear phthalin solution is kept over a small quantity of granular zinc.



The prepared phthalin was dissolved in N NaOH solution in such a manner that the solution contained 0.0585 gm. phthalin per cc. (calculated on a dry basis). This makes 1 cc. phthalin solution equivalent to 10 mg. HCN.

(2) Cu^{++} reagent was made up from pure $CuSO_4 - 5\ H_2O$ to contain 0.02354 gm. Cu^{++} per cc. This makes 1 cc. of the resulting solution equivalent to 10 mg. HCN.

(3) NaCN test solutions:

37 gr. of pure cyanide was dissolved in 2 L. of 0.1N NaOH. A standard solution of $AgNO_3$ was prepared from a weighed amount ofanalytical $AgNO_3$ (Kahlbaum). The strength of the NaCN solution expressed in mg. HCN/cc. was determined by the method of Liebig.

$$\text{Mg. HCN/cc.} = \frac{54 \times \text{cc. } AgNO_3 \times N\ (AgNO_3)}{\text{cc. NaCN}}$$

Stock solution I found to contain 9.85 mg. HCN/cc. 101.6 cc. of this solution was made up to 1 L. with 0.1N NaOH producing stock solution II, containing 1 mg. HCN/cc. By further dilution stock solution III and IV were obtained containing 0.10 and 0.02 mg. HCN/cc.respectively. The latter solution was most generally employed as 50 cc. represented 1 mg. HCN.

Procedure.

50 cc. (1 mg.) of the stock solution IV is shaken with 1 cc. phthalin reagent and 1 cc. Cu^{++} reagent added. A precipitate of $Cu(OH)_2$ is formed by the reaction of the excess Cu^{++} added and the NaOH present. The Cu. $(OH)_2$ is filtered off and the resulting depth of color noted (or compared with a standard) in a colorimeter. The colorimeter used con-

sists of a rectangular box having two holes at the top in which the tubes are inserted. At the bottom there are two holes slightly smaller than the diameter of the tubes through which light is projected into the columns of liquid being prepared. The inside of the box is painted black and glare killed by dusting it with powdered charcoal. The colors are matched by pipetting off liquid until a check is obtained. Light buff and terra cotta colored cards were found very effective in accentuating the color differences of the two columns.

The basis of all oxidation reactions involving CN^- is the liberation of nascent cyanogen, which is a powerful oxidizing agent, by the peculiarly characteristic reaction between cupric salts and the CN^- radical.

$$2\ CuSO_4 + 4\ NaCN = 2\ Na_2SO_4 + (CN)_2 + 2\ CuCN$$

When a reducing agent is present no $(CN)_2$ is liberated. The reaction in the case of the oxidation of phthalin is

$$2HCN + 2\ CuSO + HOCOC_6H_4CH(C_6H_4OH)_2 = 2H_2SO_4 + 2CuCN + OCC_6H_4\underset{O}{\underline{]}}C(C_6H_4OH)_2$$

Since the reduced dihydroxy phthalophenone was seen to be very susceptible to oxidation during its preparation, it was thought advisable to test its stability under operating conditions. Portions of the reagent exposed to the air on watch glasses colored only after prolonged exposure. Negative results were also obtained with various common oxidizing agents, e.g., HNO_3, H_2O_2, $K_2Cr_2O_7$, etc. One cc. of the reagent was placed in 100 cc. of 0.1N NaOH and air bubbled into

it rapidly for eight hours, at the end of which time the solution was perfectly colorless. However, when a stream of ozonized air (from L.O.Warner apparatus) was introduced, the solution immediately reddened. Hence, it was concluded that the material was very satisfactory from the standpoint of stability.

Phthalin reagent which had been prepared for several months was found by L.O.Warner to be more susceptible to oxidation, than the fresh material. Both positive and negative tests were obtained by the author with old reagent when the procedure was carried on in the absence of CN^- . In all cases the coloration was small. It is also of note that the two months old phthalin reagent prepared according to an abstract* of Thiery's work did not give positive tests on blank runs.

Materials other than Cu^{++} were investigated in view of their use in its place. The "ic" forms of all the common poly-valent metals were tested, and, except in the case of slight impurities of Cu^{++} , gave negative tests. Hence the test might be used as a very delicate test for Cu^{++} . Iodine was also suggested and tested. It produced a pink coloration tempered with the characteristic brown of the I_2 . The pink faded quickly, leaving only the brown.

A determination was carried out to study the influence of the order of addition of the two reagents. To 100 cc. of stock reagent IV 1 cc. Cu^{++} reagent was added and mixed thoroughly and 1 cc. phthalin reagent added. To a similar portion of stock solution 1 cc. phthalin was added, mixed and then 1 cc. Cu^{++} reagent added.

* C.A. 1 , 972.

The apparent ratios of the two equal solutions was 1 - 1.4. Hence it was concluded that it is of paramount importance that the phthalin reagent be present upon addition of the Cu^{++} .

Results of trial runs showed (1) that 1 mg. of HCN (in 50 cc.) gave the maximum density of color which was convenient to manipulate; (2) that amounts as low as 0.1 mg. HCN in 50 cc. gave a very definite color; (3) during the test runs it was noted that the color of the phenolphthalein solution faded markedly upon standing. In 1 mg. portions (100 cc.) the ratio of the fresh to two-hours-old material was found to be 1 - 0.36. This factor, of course, would constitute a very serious drawback to the use of the method as a field test. In any event, it will necessitate a repeated preparation of the color standard, if not entirely invalidate this method of analysis. It then remains a problem to be solved by trial, as to whether the color will be stable over a sufficient length of time to permit runs to be made. (4) The time of a run is materially lengthened by the necessity of filtration.

It was noted that in some of the preliminary tests the quality of the color in some pairs of tubes was not the same, i.e., a murkiness was apparent. A series of tests were undertaken to study the differences existing between the tubes and to pair off or eliminate defective tubes. A quantity of stock solution (100 cc.) was taken, the reagents added,and the solution filtered. This solution was roughly divided into two parts and the two tubes compared in the colorimeter. The liquid of one tube was then diluted to twice its volume and checks again made. Four or five similar checks were

made on each pair of tubes; the final concentration being 0.06 mg. of HCN/50 cc. It would be expected that under such ideal conditions a consistent set of results could be obtained or at least the discrepancies would be in the same direction, i.e., characteristic of a certain tube. However, it was found, after a large number of tests had been made, that this was not the case. The percent difference in heights and hence the apparent difference in amounts of HCN varied from -13% to +13% in the same set of tubes, producing an absolute difference between possible readings obtainable of about 25%. These divergences were seemingly not confined to any set of tubes or concentrations.

Conclusions.

From the foregoing preliminary work, it was concluded that this anaylsis does not for, the following reasons, warrant further work:

(1) The necessity of filtering the solution.

(2) The fading of the phenolphthalein.

(3) The erratic divergence of results.

It is impossible to avoid the use of an excess of Cu^{++} and consequently the formation of the floculent blue precipitate of $Cu(OH)_2$. The filtration of this substance is necessarily slow, thus materially reducing the speed and simplicity of analysis. Were this the only drawback in the procedure, it would not be sufficient to condemn the analysis.

The fading of color is the most serious handicap. Experiments were not carried out to determine the function of this effect with respect to time and concentrations. It certainly necessitates the frequent renewal of the color standard, if not entirely invalidating the

analysis.

In any colorimetric analysis the personal factor of the operator is a very important one. With the apparatus available, it was found impossible to obtain reliable or reproducable results. The absolute error to be expected was found in the preliminary trials to be about 25%. With a good (Dubosque) colorimeter, this factor should be almost entirely eliminated under such ideal conditions as were present in the preliminary checks on the tubes. In view of this large and erratic personal factor encountered, it was deemed useless to try to study colorimetrically the effects of fading with respect to time, of concentrations, of temperature, or of differences in heights of liquid columns.

In view of the satisfactory volumetric analyses of HCN which might be applied to the original problem, it is questionable whether (with the facilities available) this procedure warrants further development, as a quantitative analysis. It may be stated, however, that the reaction constitutes a very delicate and satisfactory qualitative test for small quantities of CN^- or Cu^{++}. One part of HCN per million parts of water is very easily recognized.